

Entropy scaling laws for diffusion

Sorin Bastea*

Lawrence Livermore National Laboratory, P.O. BOX 808, Livermore, CA 94550

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Recently, Samanta et al. [1] set out to understand the low density failure of the entropy scaling law for the self-diffusion coefficient D conjectured by Dzugutov [2] and to provide a simple alternative. After an interesting derivation, that however contains a number of uncontrolled approximations, they arrive at Eq. 7 of [1], which reduces for a hard sphere fluid to:

$$\frac{D}{D_E} = \frac{A}{1 - s_e/k_B} \quad (1)$$

with $D_E = D_B/\chi$ and $D_B = 3(k_B T/\pi m)^{1/2}/8\rho\sigma^2$ the Enskog and Boltzmann diffusion coefficients [3], χ the contact value of the pair correlation function, s_e the excess entropy per particle, and $A = 2.5$. Using the excess entropy $s_e/k_B = -(4\eta - 3\eta^2)/(1 - \eta)^2$ and contact value $\chi = (2 - \eta)/2(1 - \eta)^3$ given by the Carnahan-Starling equation of state [4] ($\eta = \pi\rho\sigma^3/6$ - packing fraction), we test this relation against the molecular dynamics simulation results of Erpenbeck and Wood (EW)[5] - Fig. 1. The disagreement is quite significant and more important the behavior of the two curves is very different, as $(D/D_E)_{EW}$ is not a monotonically decreasing function of $(-s_e/k_B)$. The discrepancy cannot be attributed to the authors use of an approximation for the excess entropy.

The idea of entropy scaling for transport coefficients has a fairly long history [6]. Arguing on the basis of the molecular ‘‘caging’’ effect Dzugutov [2] proposed the scaling law:

$$\frac{D}{\sigma^2 \Gamma_E} = B \exp(s_e/k_B) \quad (2)$$

which assumes that the natural length and time scales for diffusion are given by a suitably defined hard sphere diameter σ and the Enskog collision frequency $\Gamma_E = 4\sigma^2\chi\rho\sqrt{\pi k_B T/m}$, with B an universal constant. Unfortunately, the above relation appears to work only in a limited, high density domain for both hard spheres [7] and realistically modeled fluids [8]. The problem that arises at low and moderate densities (see Fig. 1) with the scaling introduced in Eq. 2 can be understood if we observe that the left-hand-side of that equation can be written up to a multiplicative constant as $D/D_B\chi\eta^2$. Therefore, in the limit of a dilute system, $\eta \rightarrow 0$, this term diverges as $1/\eta^2$, while the right-hand-side of Eq. 2 remains finite. This behavior should be expected for any valid definition of σ and χ and s_e approximation. The noted pathology of Eq. 2 can be avoided by replacing σ as the relevant length scale with $1/\rho\sigma^2$, the Boltzmann mean-free path, which should be a reasonable measure of the degree of molecular confinement, $1/\rho\sigma^2 \propto \sigma/\eta$. The new relationship is:

$$\frac{D}{D_B\chi} = \exp(\gamma s_e/k_B) \quad (3)$$

where we introduced a different constant γ . The test of this dependence is shown in Fig. 1 for hard spheres, with $\gamma = 0.8$. Furthermore, Eq. 3 holds for Van der Waals fluids as well [8].

Samanta et al. also propose a generalized Stokes-Einstein relation. However, such a relation is hardly necessary given that the usual Stokes-Einstein formula with the ‘slip’ boundary condition holds well for both hard spheres [9] and Van der Waals fluids [8].

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* Electronic address: bastea2@llnl.gov

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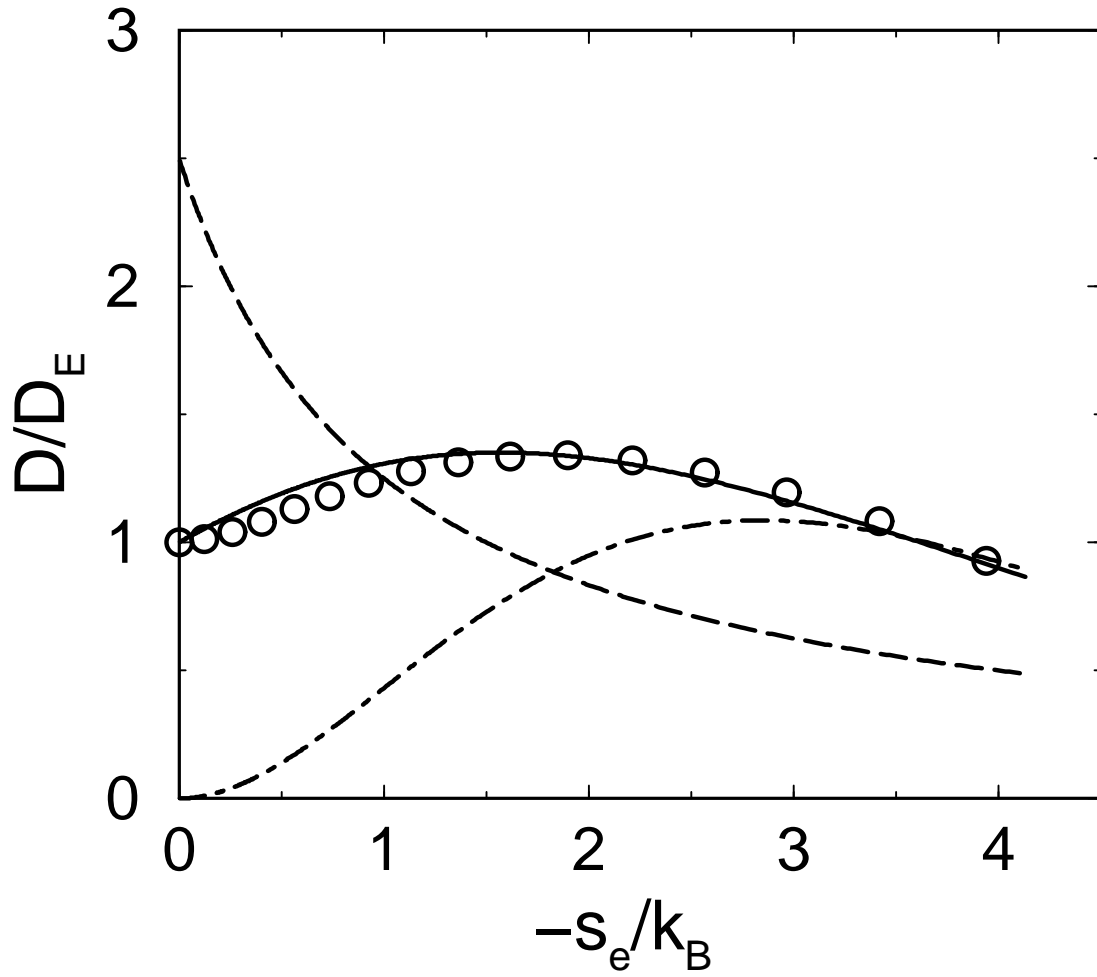


FIG. 1: Comparison of the hard spheres diffusion coefficient (Ref. [5]) - circles, with scaling relation of Ref. [1] (Eq. 1) - dashed line, Dzugutov scaling law [2] (Eq. 2) - dot-dashed line, and new entropy scaling (Eq. 3) - solid line.

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